

Technology Base Studies of Long-Term MCFC Performance

CONTRACT INFORMATION

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OBJECTIVES

The separator plate/current collector of the molten carbonate fuel cell (MCFC) has various contact areas with the carbonate melt. The wet-seal area resembles most closely the fully immersed condition. On the other hand, areas exposed to the gas channels can be dry or covered with a thin film due to creeping of the melt from the porous electrode onto the separator or current collector.

A compact (thin) and dual-structured oxide layer is required for good corrosion protection by any candidate material, regardless of degree of wetting.

Electrochemical aspects of the corrosion process on stainless steels 310 and 316L were presented in the previous contractors meeting [1]. Fig. 1 shows schematic of possible electrode configurations for carbonate wetting.

BACKGROUND

It is well-known that in the corrosion of stainless steel by molten carbonate chromium forms a protective layer or surface oxide scale which causes the substrate not to be further oxidized. The chromium content of the alloy determines whether it forms an interior layer or an external

scale. Low oxide diffusivity in the oxide scale can cause chromium to diffuse to the surface. While chromium is oxidized to form Cr_2O_3 at the metal/oxide interface, an FeO layer also forms and may grow at higher rates. A quantitative explanation of the oxidation behavior of alloy systems requires dealing with multi-component diffusion.

PROJECT DESCRIPTION

This project aims to identify the long-term endurance problems of the MCFC by investigating corrosion of stainless steel (i.e., 310 and 316L). Although the corrosion resistance of stainless steel Type 310 is better than that of Type 316, the poorly conducting surface oxide layer on Type 310 is a source of significant ohmic resistance in long term operation, where a layer that is not only corrosion resistant but also conductive is needed. Electrochemical measurements show significant differences in corrosion behavior between completely submerged samples and samples wetted by a carbonate film. This presentation will focus on the results from SEM and cross-section analysis.

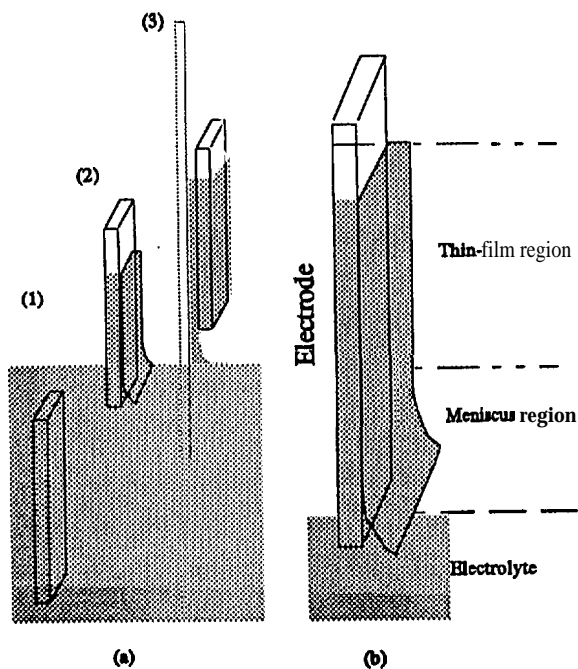


Figure 1. (a) Possible electrode configurations in the electrolyte:(1) fully, (2) partially immersed and (3) thin-film wetted, (b) detail of partially immersed electrode configuration

RESULTS

Steady-state polarization

The open circuit potential of the Type 310 as well as Type 316L steel under CO_2 becomes stable around -1000 mV. The stable potential under CO_2 shows roughly 50 mV potential difference between a fully immersed and a mounted electrode. Under CO_2 , these surfaces are indeed stable (i.e., no surface reaction is observed). Table 1 shows corrosion currents and potentials derived from log I-E plots. The data suggest a lower corrosion resistance for thin-film covered electrodes than for immersed electrodes with higher corrosion resistance of Type 310 steel.

Table 1. Corrosion currents from steady-state polarization plots under CO_2

sample	immersed E_{CORR} , mV	immersed I_{CORR} , μA	thin-film E_{CORR} , mV	thin-film I_{CORR} , μA
SS310	-1023	4.1	-986	29.6
SS316	-1040	23	-981	40

Surface-layer analysis

The corrosion surface and the layers found on Type 310 and Type 316L steels by cross-section are compared for the effect of carbonate on the formation of corrosion products. In the case where the stainless steel 310 is fully immersed in the carbonate mixture, the most inner layer depleted in Fe and Ni is mainly chromium oxide. Chromium content gradually decreases from bulk metal to the metal/electrolyte interface. Since Fe diffuses to this interface to form a thick oxide surface layer, the layers below the surface are richer in Cr.

Layers formed with a thin-film wetted configuration show concentration differences at the top and the bottom of the electrode, at the gas-facing as well as ceramic-facing side. At the bottom, the most outer layers are continuous and Cr and Fe rich. Below this, a region rich in Fe and Ni occurs. Between this layer and the metal/oxide interface, spreading of chromium oxide is observed. At the top, fewer layers can be distinguished by microprobe analysis. In both gas and ceramic-facing sides, the layer just below the surface is very rich in Cr. At the top of the sample, the overall thickness of the oxide layer becomes less. The more strongly wetted side (ceramic-facing) has a ~ 10% thicker oxide layer than the gas facing side. The thicknesses are given in Table 2.

Figures 2(a), (b), (c) and (d) show map analyses of oxide layers on thin-film wetted electrodes at the ceramic-facing side. An approximately 8 μ thick iron rich surface layer is observed (b). The region below that is about 6 μ thick and rich in chromium (d). The thickness of the most interior Cr_2O_3 layer is ~5 μ and consists mostly of Fe and Ni oxides. Open areas around the dark regions (a) are iron and nickel. Concentration profiles for immersed and thin-film covered electrodes are given in Figures 3(a), (b).

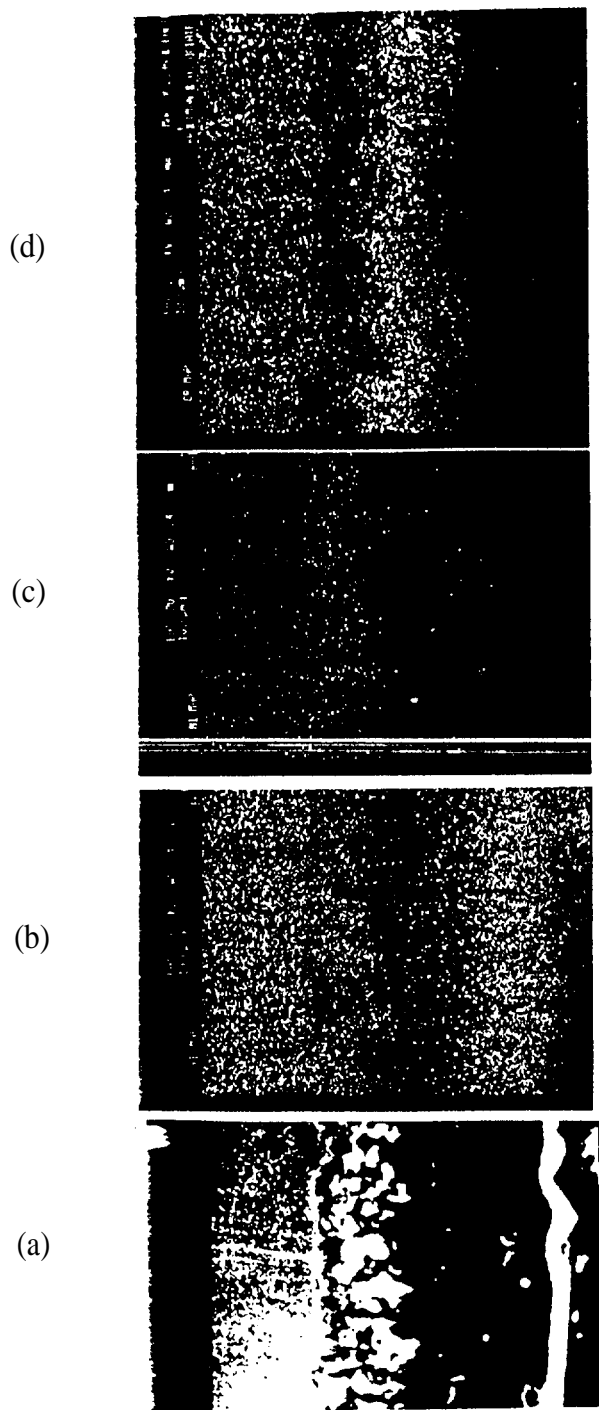


Figure 2. Map analysis on the (a)cross-section of thin-film covered 310 for (b) Fe, (c)Ni, (d)Cr

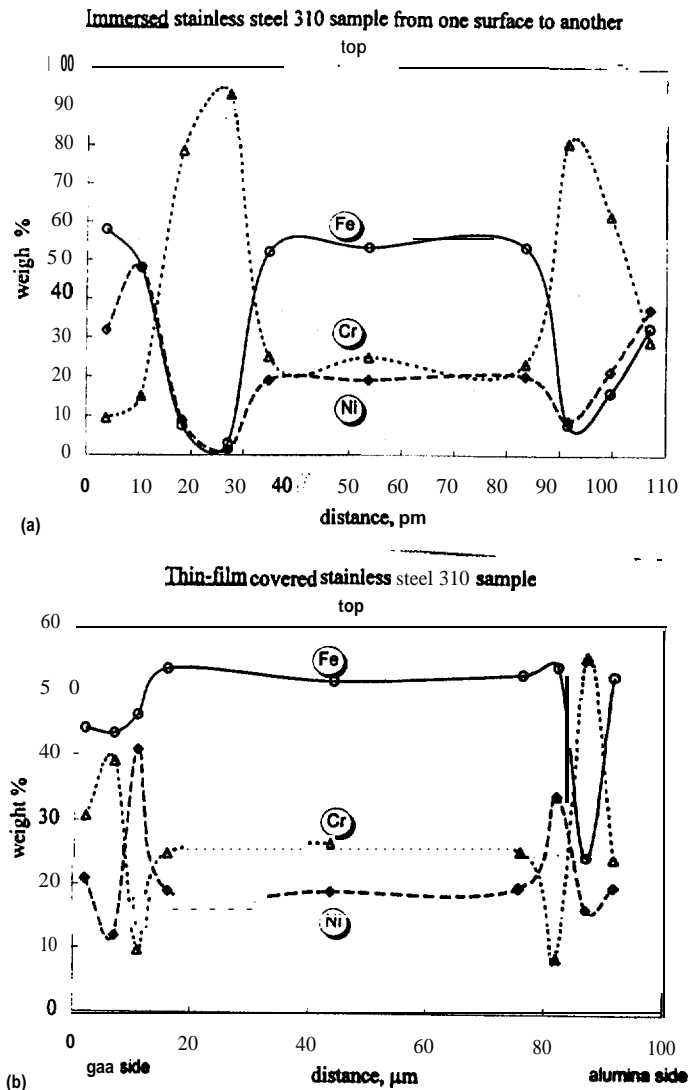


Figure 3. Concentration profiles at the cross-section of (a)immersed and (b)thin-film covered Type 310 stainless steel

Table 2, Thickness of the oxide layers on stainless steel 310

sample	thickness, μ		thickness, μ		thickness, μ	
	top		middle		bottom	
	outer	inner	outer	inner	outer	inner
FE	13	15	14	18	19	22
IE			31		25	

The schematic of corrosion layer formation on immersed and thin film covered alloys is shown in Figure 4.

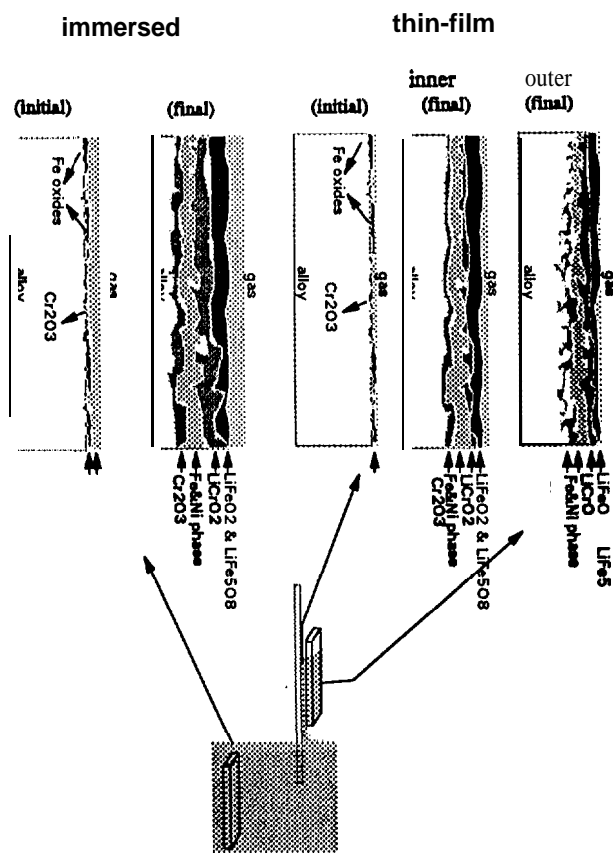


Figure 4. Schematic of initial and final layer configuration on stainless steel 310

CONCLUSION

Significant differences observed in this study between immersed and film-wetted electrodes are summarized below

- (1) The observed OCP decay of alloys suggests that higher chromium and nickel content helps the formation of a more protective, continuous sub-scale. In Type 316L, iron may diffuse outward and break the thin Cr_2O_3 protective scale. Thereby, lithium may more easily diffuse into the alloy and Fe or Cr cations may diffuse toward the oxide/electrolyte interface, facilitating corrosion.
- (2) A compact(thin) and dual-structured oxide layer is required for good corrosion protection by any candidate material, and this is affected by the degree of wetting. The film-wetted alloy forms a

much more compact layer, due to the passive surface oxide formed under high oxygen activity, than the same alloy immersed in a deep layer of carbonate. The corrosion layer thickness close to the bulk melt is thicker than at the top of the sample where it is only slightly wetted. Surface contacting a thin carbonate film forms a spreading Cr_2O_3 layer while a deeply immersed surface forms a continuous inner layer of Cr_2O_3 much more slowly and less reliably.

(3) The corrosion protection provided by the film wetted electrode is related to convection at the melt/oxide interface(via the meniscus) and to gas access(via the film). The potentials of thin-film covered samples approach the oxygen reduction potential within a few hours. This is explainable by easy access of oxygen to the metal/electrolyte interface. A protective scale forms before lithium ions penetrate and can take part in the corrosion process. When electrodes are fully immersed, the diffusion of lithium into, and of cations(Fe, Ni and Cr ions) out of, the alloy overtakes the oxide layer formation process. Alloy inter-diffusion coefficients, therefore, are important in comparing and understanding the corrosion behavior of stainless steels and alloys,

FUTURE WORK

These results suggest that pre-oxidation can be a solution to obtain a compact oxide layer. Adding Al to alloy leads to a very stable oxide layer, but increases its resistivity. Alloy behavior must also be investigated under continuously polarized conditions, for more realistic corrosion predictions.

REFERENCES

- [1]. J. R. Selman and M.S. Yazici, "Technology Base Studies of Long-Term MCFC Performance", Proceedings of the Fuel Cells '95 Contractors Review Meeting, 1995